



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : D21H 19/60	A1	(11) International Publication Number: WO 92/01836 (43) International Publication Date: 6 February 1992 (06.02.92)
(21) International Application Number: PCT/GB91/01181 (22) International Filing Date: 17 July 1991 (17.07.91) (30) Priority data: 9015844.5 19 July 1990 (19.07.90) GB (71) Applicant (for all designated States except US): VINAMUL LIMITED [GB/GB]; Mill Lane, Carshalton, Surrey SM5 2JU (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): BOODAGHIANS, Razmik, Baghdassar-z [GB/GB]; 37 Carshalton Grove, Sutton, Surrey SM1 4LY (GB). FARMER, David, Bretland [GB/GB]; Spring Cottage, Sutton Place, Abinger Hammer, Dorking, Surrey RH5 6RP (GB). PHILLIPPS, Roy, Gordon [GB/GB]; 10 Forge Rise, Uckfield, East Sussex TN22 5RU (GB).		(74) Agent: ROSCOE, Brian, Corrie; Patent Division, Unilever plc, Unilever House, Blackfriars, London EC4P 4BQ (GB). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COPOLYMER EMULSION FOR PAPER COATING (57) Abstract A copolymer emulsion used for paper coating and based on vinyl acetate is given improved wet pick strength incorporating vinyl esters of tertiary branched carboxylic acids.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU ⁺	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

⁺ It is not yet known for which States of the former Soviet Union any designation of the Soviet Union has effect.

COPOLYMER EMULSION FOR PAPER COATING

FIELD OF THE INVENTION:

This invention relates to aqueous emulsions containing copolymers of vinyl acetate in which vinyl acetate is the major component. Copolymers of the invention are utilised in paper and board coating compositions and demonstrate good rheology and dry pick strength with enhanced wet pick strength. The term 'paper' is used herein to include board substrates.

BACKGROUND OF THE INVENTION:

Paper coating compositions usually comprise an aqueous polymer binder emulsion, a pigment and optionally other additives common in the technology. The present invention is specifically directed to novel emulsions based on copolymers comprising a vinyl C1 to C4 alkanoate component forming at least about 60% by weight of the copolymer, more usually at least about 70% by weight and an alkylene component, e.g. ethylene. Vinyl acetate is an example of a vinyl ester of a C1 to C4 alkanoic acid to which the invention is generally directed. Coating compositions of the invention will contain a pigment, for example clay, which is compounded with the latex binder and used in coating a cellulosic web for example a paper or paperboard web. The characteristics of the latex binder component are significant in the ease of preparation of the paper coating composition, its application and on the qualities of the coated product.

The coating composition will be coated on to a paper substrate surface, dried and calendered. Usually the composition will be applied at a level to give a loading

of about 18 to about 24 g/m² solids on one surface. The copolymer particles will bind those of the pigment filler to provide cohesive strength and contribute to the adhesion between the coating and paper substrate. The coating, which will usually have a thickness of about 3 microns to about 10 microns, imparts gloss and whiteness to the paper and provides a suitable surface for receiving ink.

When the coating is subjected to successive printing operations, for example in offset lithography, the coating must provide acceptable wet and dry pick strengths. When the first colour is printed any pull by the tacky ink giving failure of the coating is termed 'dry pick'. Failure when the coated paper passes to the second inking stage, when ink is applied to prewetted areas, is termed 'wet pick'. Subsequent inking steps can also give rise to wet pick failure.

General description of the Invention:

The invention provides the use in paper coating of an aqueous copolymer emulsion having a solids content from about 20% to about 70% by weight and comprising

- i) from about 60%, preferably from about 70%, to about 99% by weight of a vinyl C1 to C4 alkanoate, and
- ii) from about 1% to about 40% by weight, preferably from about 5% to about 25% by weight, of vinyl esters having the general formula $R_1R_2R_3\text{CCOOCHCH}_2$ wherein R_1R_2 and R_3 are each alkyl groups having at least one carbon atom and $R_1+R_2+R_3$ is from 3 to 9.

This product has good rheology and dry pick strength and enhanced wet pick strength which is attributable to the presence of vinyl ester (ii) monomers. There is a general requirement in paper coating to improve these characteristics.

The invention extends to a pigmented paper coating composition comprising

- i) to 100 parts of pigment and
- ii) from about 3% to about 30% by dry weight of an aqueous emulsion as defined above.

In the emulsions prepared for use in paper coatings the polymerisation system will be substantially free of protective colloids. Colloidal materials may be added subsequently to the paper coating composition.

Although vinyl acetate is the preferred vinyl alkanoate monomer because of its availability, cost and known reactivity, other vinyl esters within the class defined are usable in particular vinyl formate, propionate, butyrate and isobutyrate.

Optionally the copolymer may contain minor monomer components added to provide specific benefits, examples are sodium vinyl sulphonate, acrylic acid, methacrylic acid, acrylamide, hydroxy functional acrylates, vinyl silanes and vinyl halides. A favoured comonomer is a polyethylenically unsaturated compound selected from triallyl cyanurate, triallyl isocyanurate, diallyl maleate, diallyl fumarate, divinyl benzene and diallyl phthalate.

Methods for preparing the copolymer emulsions of the invention are well characterised in the literature. Polymer Synthesis (vols I and III) by Sandler & Karo (Academic Press 1974) and Preparative Methods of Polymer Chemistry (2nd Ed) by Sorenson and Campbell (Interscience 1968) provide preparative information. Methoden der Organischen Chemie (Houben-Wey) Band XIV published by George Thieme Verlag Stuttgart (1961) also provides preparative descriptions.

Preferably at least one surfactant used in the polymerisation process contains a C14 to C20 alkenylene, i.e. unsaturated, moiety and examples are an oleyl propanol amide sulphosuccinate obtainable from Witco of USA under the trade name Emcol K8300 and the potassium salt of the sulphonation product of oleic acid obtainable from Lankro Chemicals of Manchester England under the trade name Lankropol OPA.

The paper coating composition comprises a pigment, for example clays, hydrated silica clays, and other conventional ingredients. The clays used include Kaolin group clays and hydrated silica clays, specific clays are disclosed in "Kaolin Clays and their Industrial Uses" by J. M. Huber Corp. (1949) New York chapters 10 to 16.

Other pigments, for example calcium carbonate, titanium dioxide, blanc fixe, lithopone and zinc sulphide may be used in addition to clay. In general the paper coating composition will comprise

<u>Component</u>	<u>Parts by weight</u>
Pigment	100
dispersing agent eg. sodium pyrophosphate	0.1 to 0.5
latex (on solids basis)	3 to 30
Cobinder e.g. starch or casein	0 to 25
Defoamer, e.g. a hydrocarbon oil	0 to 0.2
Water to provide desired solids level.	

The coating compositions produced with the aid of the latexes of the invention will be applied to fibrous paper webs using conventional means for example trailing blade coaters, air knife coaters and roll coaters.

Literature

The applicants are aware of the following disclosures relating to polymer emulsions.

EPA 0295727 (Shell) describes polymer emulsions containing vinyl acetate, ethylene and versatates (Veova 9) for use in paint compositions to give non tacky surfaces which are alkali resistant. These benefits are demonstrated in comparison with Veova 10. The description suggests the emulsions are usable in paper coating and other fields, but there is no disclosure of the wet pick benefit identified in the present application.

EPA 0172354 (Air Products) describes vinyl alkanoate/ethylene emulsions for paper coating which provide enhanced dry pick strength and gloss. The additional monomers are unsaturated acids/esters and dicyclopenta-dienyl acrylate. Vinyl versatates are quoted as examples of the alkanoates but there is no suggestion to use them as a third monomer with VA/E. VA/E is stated

to lack sufficient wet pick resistance for offset printing.

GB 1144316 (Dunlop) describes alkali-soluble polymer emulsions formed from quaternary alpha carbon carboxylic, vinyl carboxylate and unsaturated carboxylic monomers. pH and viscosity stability derive from the tertiary monomer.

Test Methods:

- i) Dry pick strength values (cm/sec) were measured using a coating composition on Reeds Aircoat woodfree paper using an IGT Dynamic Pick Tester (AC2 Model) with 25 Kg load and low viscosity ink. The composition tested contained:

Pigment SPS clay*	to 100 parts
Emulsion under test	24 parts of 50% solids emulsion
Water retention aid** Finnfix FF5	0.5 parts
Dispersant*** Dispex N40	0.3 parts
Sodium hydroxide	0.15 parts
Water to give 45% solids	

* obtainable from English China Clay of St Austell England.

** Obtainable from Finn Forest Chemicals of Cheam, England.

*** Allied Colloids of Bradford, England.

- ii) The wet pick strength was measured with the apparatus of the dry pick method. 0.3 mls of ink was applied

to each roller and distributed for 15 minutes. A test strip of paper coated with the test composition to a level of 20g/m² (solids) was placed in the device. The inked roller was contacted with the test strip and adjusted to a printing force of 35 Kgf. A drop of tap water was placed on the test strip immediately in the path of the roller so ink is applied over a layer of water spread by progress of the roller.

The degree of resistance to pick is judged at a qualitative level i.e. good - fair - bad.

SPECIFIC DESCRIPTION OF THE INVENTION

Examples of the invention will now be given to illustrate but not limit the invention. The formulation used in Example I was:

FORMULATION

Initial Charge:

distilled water	1092.0g
Emcol K8300 (as 37% aq soln)	61.6g of active
Aerosol A102 (as 30% aq soln)	44.1g of active

Monomers:

Vinyl Acetate (VA)	1022.0g
Veova 9** (VV9)	256.0g
Silane A172	6.1g
Diallylmaleate	2.6g

Distilled Water	25.0g
Ammonium Persulphate	8.0g

Distilled Water	40.0g
t-butylhydroperoxide (TBH)	3.8g

Distilled Water	40.0g
Sodium Metabisulphite	3.8g

pH adjusted to be 7 to 8 with 25% ammonium hydroxide.

** VeoVa 9 is vinyl ester of versatic acid in which $R_1 + R_2 + R_3 = 7$ and is obtainable from Shell Chemicals of Chester England.

Emcol K8300 is sodium oleyl propanol amide sulphosuccinate obtainable from Witco of USA.

Aerosol A102 is the disodium salt of an ethoxylated alcohol half ester of sulphosuccinic acid obtainable from Cyanamid of Wayne New Jersey USA.

Example I

The initial charge containing the surfactants was loaded into a stirred 5 litre vessel and heated to 70°C under nitrogen. 10% of the monomers was then added followed by 45% of the ammonium persulphate catalyst solution. The temperature was then raised to 75°C over 45 minutes.

At 75°C the remainder of the monomers began to be added over a period of 5 hours. 30 minutes after beginning this addition the remaining 55% of the persulphate catalyst was added over a period of 5 hours. During the monomer addition the temperature was maintained at 75°C.

After completing the monomer addition the temperature was raised to 80°C and maintained at this temperature for 45 mins, i.e. 15 mins after catalyst addition finished.

The reaction mixture was then cooled to 50°C and the finishing off solutions of TBH and metabisulphite added. The product emulsion was then cooled and filtered. Ammonia solution was used to adjust the product pH to be between 7 and 8.

Examples II to VI

Additional examples were performed using the process steps of Example I but varying the quantities of the base monomers, i.e. vinyl acetate, VeoVa 9 and, replacing VeoVa 9 with VeoVa 5, which is vinyl pivalate. In this material R_1 , R_2 and R_3 are each methyl i.e. $R_1+R_2+R_3=3$. These emulsions were also tested for wet and dry pick strengths.

The emulsion products had solids contents comparable to that obtained in Example I i.e. in the range 49 to 51%.

The result of the dry and wet pick tests on a coating composition containing the resulting emulsion are given in Table I.

The applicants have found the addition of a vinyl ester of the class exemplified by VeoVa 9 (VV9) or VeoVa 5 (VV5) to a vinyl acetate emulsion polymer system improves the wet pick resistance of a paper coating composition. Equivalent results are found when the $R_1+R_2+R_3$ sum is 4 or 5.

TABLE I

Example	VA	VV9	VV5	Pick strength	
				<u>Dry</u>	<u>Wet</u>
I	80	20	0	56	Fair/good
II*	100	0	0	70	Fair/poor
III	98	2	0	73	Fair
IV	90	10	0	64	Fair/good
V	90	0	10	70	Fair
VI	80	0	20	63	Fair

* control emulsion.

WHAT WE CLAIM IS:

1. The use in paper coating of an aqueous copolymer emulsion having a solids content from about 20% to about 70% by weight and comprising
 - i) from about 60% to about 99% by weight of a vinyl C1 to C4 alkanooate, and
 - ii) from about 1% to about 40% by weight, preferably from about 5% to about 25% by weight, of vinyl esters having the general formula $R_1R_2R_3CCOOCHCH_2$ wherein R_1R_2 and R_3 are each alkyl groups having at least one carbon atom and $R_1+R_2+R_3$ is from 3 to 9.
2. A pigmented paper coating composition comprising
 - i) to 100 parts by weight of pigment, and
 - ii) from about 3 parts to about 30 parts by dry weight of an aqueous emulsion as defined in claim 1.
3. A pigmented paper coating composition as claimed in claim 2 further comprising:

from about 0.1 to about 0.5 parts of dispersing agent,
from 0 to about 2.5 parts of cobinder,
from 0 to about 0.2 parts of defoamer, and
water to appropriate level.


4. A process of offset lithographic printing of paper wherein the paper surface is coated with the composition of claim 2 prior to printing.

5. A process as claimed in claim 4 wherein the composition is applied at a level to give about 18 g/m^2 to about 24 g/m^2 dry solids.

INTERNATIONAL SEARCH REPORT

International Application

PCT/GB 91/01181

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 D21H19/60		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	D21H	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,X	WD,A,9 008 853 (UNILEVER P.L.C.) 9 August 1990 see the whole document ---	1-5
X	US,A,4 657 821 (S.URA ET AL.) 14 April 1987 see abstract see column 3, line 53 - column 4, line 23 ---	1-5
X	EP,A,0 315 278 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 10 May 1989 see abstract see page 4, line 36 - line 37 ---	1
A	EP,A,0 295 727 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 21 December 1988 cited in the application ---	
<p>¹⁰ Special categories of cited documents: 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"T" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
25 NOVEMBER 1991	15. 01. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	SONGY 04110 	

Form PCT/ISA/210 (second sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. GB 9101181
SA 49467**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 25/11/91

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9008853	09-08-90	AU-A- 4965790 EP-A- 0381379	24-08-90 08-08-90
US-A-4657821	14-04-87	JP-A- 59223396	15-12-84
EP-A-0315278	10-05-89	JP-A- 1149811	12-06-89
EP-A-0295727	21-12-88	None	

EPO FORM P0679

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82